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SLIDING WEAR RESISTANCE AND MICROHARDNESS OF EPOXY CLAY NANOCOMPOSITE COATINGS

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ABSTRACT

Epoxy clay nanocomposites were prepared by ultrasonication and were applied on flat and cylinder or pin shaped mild steel specimen for microhardness and sliding wear resistance test, respectively. The optimum thickness of coating that doesn't experience any substrate effect when indented was determined to be 200 microns. Microhardness was optimized by conducting microhardness tests as per Taguchi's technique (L9 orthogonal array). The input factors influencing the microhardness were nanoclay concentration (wt.%), sonication time (minutes), and curing time (days). From the main effects plot, it was observed that microhardness increases with increase in nanoclay concentration. As sonication time increases from 5 to 10 minutes, microhardness increases. But when sonication time increases from 10 to 15 minutes, microhardness decreases. The microhardness is maximum for a curing time of 3 days. The optimum levels of the three factors were 5 wt % of nanoclay, 10 minutes of sonication time and 3 days of curing. Nanoclay concentration was the most influencing factor followed by sonication time and curing time. The obtained output data was used to fit in a regression equation. Sliding wear resistance test was carried out using a pin on disc wear testing machine. Sliding wear resistance increases with increase in nanoclay concentration till 4 wt %. The sliding wear resistance does not change beyond 4 wt % which is due to agglomeration of nanoclay.

KEYWORDS: *Epoxy Clay Nanocomposite Coating, Substrate Effect & Microhardness*

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Original Article

INTRODUCTION

Epoxy resins are used as coatings due to their high chemical resistance [1–3], good barrier properties [1], strong adhesion to substrates [1–3], good electrical insulating properties and outstanding process ability [2–3]. However, they possess some disadvantages such as brittleness [2], low fracture toughness [2], susceptible to damage caused by abrasion and wear and poor resistance to crack initiation and propagation [2–4]. These disadvantages hinder their applications when exposed to water, oxygen, and ions for long term [1]. There is a less amount of research that shows that the addition of nanoclay to epoxy coating, the abrasion resistance [5, 7 & 8], hardness [6, 8], scratch resistance [7] and impact resistance [3] enhances. Also, clays are found to be one of the ideal nano-reinforcements for epoxy, because of its high intercalation chemistry, high aspect ratio, ease of availability and low cost [9]. In the measurement of mechanical properties of the coating, while measuring the indentation hardness there is a possibility that the substrate hardness might influence the measurement. This effect is called "substrate effect" and can be eliminated if the indentation depth is within 10% of the coating thickness [10]. The current work focuses on 1) analyzing the effect of coating thickness on the substrate effect and 2) optimization of microhardness of epoxy clay nanocomposite coating using Taguchi's optimization technique wherein the control factors considered are nanoclay concentration, sonication time and curing time and 3) evaluation of sliding wear resistance of the coating.

MATERIALS AND PREPARATION OF EPOXY CLAY NANOCOMPOSITE

In this study, epoxy resin CR120 supplied by Prime speciality coatings private limited, India was used with an epoxy equivalent weight of 189 Eq/kg. The curing agent was a cycloaliphatic hardener with phr with epoxy being 50–60. Therefore, epoxy and curing agent are to be mixed in the ratio of 2:1 as per the manufacturer's instructions. The nanoclay was supplied by Durga Lab equipment suppliers, Mangalore which was manufactured by Sigma Aldrich. The as buying nanoclay was already surface modified by 0.5–5 wt.% aminopropyltriethoxysilane and 15–35 wt.% octadecylamine.

Nanoclay in weight percentage (wt. %) was added to the epoxy resin and was sonicated using a probe type ultrasonicator. The centrifuge tube containing the mixture was immersed in a beaker containing ice bath throughout the process in order to avoid the overheating of the polymer. After sonication, the stoichiometric quantity of curing agent was added and the mixture was manually stirred for 2 minutes.

APPLICATION OF COATING ON SUBSTRATES

For measuring the microhardness of the coating, mild steel substrates of the size 110×110×2mm were prepared using emery papers to obtain a clean and smooth surface before the application of the coating. The prepared nanocomposites were applied on mild steel substrates using a four-sided wet film applicator as per ASTM standard D823-18. The process of applying the coating on the substrate is shown in Figure 1 and is also enlisted below:

- The substrate is placed on a firm glass plate
- Film applicator is placed on one end of the substrate
- A small quantity of the nanocomposite is injected in front of the applicator
- The applicator is smoothly pulled along the length of the substrate

For measuring the sliding wear resistance, mild steel pins of diameter 8 mm and length 30 mm with well-prepared surface were used. In order to coat the surface of the pin using film applicator, a fixture was fabricated that could hold multiple pins at a time, as shown in Figure 2. After the pins were inserted into the holes, the surface of the fixture was masked with only the pin surface area exposed. Nanocomposite was applied over the surface, mask was removed and the pins were left in the fixture for curing.

Figure 1: Process of Applying the Coating using Film Applicator.

Figure 2: Fixture for the Pins.

METHODOLOGY

Microhardness of coatings were measured using Micro Vicker's hardness tester. The process of measuring the microhardness involves indenting the specimen surface with square based pyramid type diamond indenter. The indenter has an angle of 136° between two opposite faces. A load of 100gf is applied for about 15 seconds against the coating surface. The micro Vicker's hardness number, HV is calculated from the equation (1)

$$HV = 1.854\frac{L}{d^2} \quad (1)$$

,where, L is load measured in grams and d is equal to the length of the diagonal measured from corner to corner on the residual impression in the specimen surface in microns (Figure 3).

The hardness tester records the values of load and diagonal and automatically calculates the hardness number HV and displays in the screen. The screen also displays the values of two diagonals, load applied, dwell time, etc.

Microhardness of coatings applied on the mild steel substrates cannot be measured and recorded directly. This is because of the substrate effect. When an indenter penetrates into the coating of a coating-substrate system, the influence of the substrate on the measured microhardness is more as the indenter penetrates further [11]. As the penetration depth, h increases the influence of the hardness of the substrate is more. Therefore, it is important to find the optimum thickness of coating, the microhardness of which doesn't get influenced by that of the substrate.

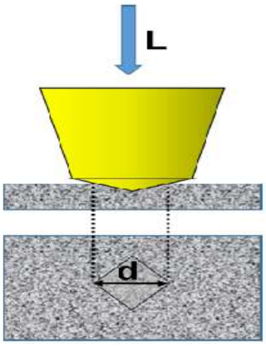

Figure 3: Vicker's Microindentation Test (Source: Broitmanet a. [11]).

For the present coating-substrate system, experiments were conducted in order to evaluate the influence of the substrate on the microhardness for different thickness of the coating. In the first set of experiment, coatings of different thickness, viz. 50,100,150 and 200 microns were coated over mild steel substrates and microhardness were measured and recorded. In second set of experiment, diagonal lengths for indentation of coatings of different thickness were noted and using the equation 2, indentation depth was calculated. Using these two sets of data, substrate effect was evaluated for all four thicknesses and optimum thickness which gives nil substrate effect was found out.

Diagonal length, d = 7×hequation (2)

Where, d is average of two diagonals

The coating with optimum thickness was used to optimize the microhardness using Taguchi's technique

Experimental Design

Taguchi's method is a powerful tool for parameter design which is used to maximize the microhardness of epoxy clay nanocomposite coatings. Taguchi's parameter design can optimize the performance characteristics through the setting of design parameters and reduce the sensitivity of the system performance to the source of variation. The microhardness test on the coatings was carried out under different operating conditions considering three factors, viz., sonication time, nanoclay concentration and curing time each at three levels as listed in Table 1 in accordance with L9 orthogonal array as per the design of experiments. The impact of these three factors was studied using L9 orthogonal design. The tests were conducted as per the experimental design at room temperature. In conventional full factorial experiment design, it would require 3^3 = 27 runs to study the three factors each at three levels, whereas, Taguchi's factorial experiment approach reduces it to only nine runs offering a great advantage in terms of experimental time and cost. The characteristic is that the higher value represents a desired response; the higher the better is used. The S/N ratio can be calculated as a logarithmic transformation of the loss function from the equation (3).

$$\frac{S}{N}\text{ratio} = -10 \times \log_{10}\left[\frac{1}{n}(y^2)\right] \quad (3)$$

where y represents the response microhardness and n denotes the number of experiments.

Measurement of Sliding Wear Resistance

Pin on disc machine was used to perform the sliding wear resistance test as per ASTM 99-17. Figure 4 shows a pin on disc machine with a specimen pin attached on to the fixed arm loaded to the disc. The system consists of a driven spindle and chuck for holding the revolving disc, a lever-arm to hold the pin, and attachments to allow the pin specimen to be forced against the revolving disc with a controlled load.

Table 1: Control Factors and Levels

Control Factors	Level 1	Level 2	Level 3
Sonication time (minutes)	5	10	15
Nanoclay concentration (wt. %)	1	3	5
Curing time (days)	3	5	7

Figure 4: Pin on Disc Machine.

The parameters set for the experiment were load of 5 N, rotational speed of the disc of 100 rpm, track diameter of 60 mm and the experiment was run for 4 minutes. The specific wear rate was measured using weight loss method from the equation (4).

$$W = \frac{\Delta w}{L\rho F} \quad (4)$$

where, W is specific wear rate measured in mm3/N-m

L is sliding distance which is equal to time×rpm×circumference in metres

ρis density of the coating material in gm/mm3

F is the load applied in N

Δw is difference in weights in grams

$$Wear\ rate = specific\ wear\ rate \times load \quad (5)$$

$$Wear\ resistance = \frac{1}{Wear\ rate} \quad (6)$$

wear resistance in m/mm^3 is calculated using equation (6) and (5)

RESULTS AND DISCUSSIONS

Study on Substrate Effect

One of the objectives of the work was to analyze the substrate effect of the coating. The analysis will lead to the minimum thickness for which there is no substrate effect. In first set of experiment, microhardness of coating of four different thicknesses were measured and plotted in Figure 5. It can be observed that, as the thickness increases, the microhardness values decrease and it starts to saturate. The microhardness value is very high for 50 and 100 microns thick coating because there could be a substrate effect. Also, it can be noted that the microhardness reduces drastically at 150 microns. The difference in microhardness between 150 and 200 microns thick coating is very small. Two-hundred microns thick coating could be the one without any substrate effect. This can be proved by the relationship given in equation (2) and Bückle's rule [10]. From equation (2) it is possible to calculate the indentation depth (h), which according to Bückle's rule must be within 1/10th of the coating thickness in order to have no substrate effect.

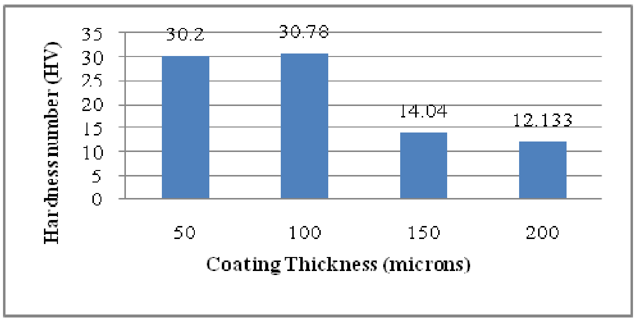

Figure 5: Variation of Microhardness with Respect to Coating Thickness.

Table 2: Diagonal Lengths for Different Coating Thicknesses

Coating Thickness (microns)	Diagonal Length (D1 in microns)	Diagonal Length (D2 in microns)	Average Diagonal Length (microns)
50	78.3	78.7	78.5
100	77.58	77.4	77.49
150	114.09	114.83	114.46
200	123.33	123.82	123.06

Experiments were carried out for different coating thicknesses, diagonal values were recorded (Table 2) and indentation depths were calculated. The diagonal value which gives an indentation depth less than 1/10th of the total thickness is said to be the one without any substrate effect.

For 50 microns coating thickness, average diagonal length = 78.5 microns. Therefore indentation depth h = d/7 = 11.2 micron which is greater than 1/10th of the total thickness (i. e. 5 microns). For 100 microns, h = 77.4/7=11 microns which is also greater than 1/10th of the total thickness (i. e. 10 microns). For 150 microns, h = 114.46/7= 16.3 micron which is also greater than 1/10th of the total thickness (i. e. 15 microns). For 200 microns, h = 123.06/7= 17.58 micron which is less than 1/10th of the total thickness (i. e. 20 microns). Therefore, a coating substrate system wherein the coating thickness is 200 microns there is no substrate effect.

Optimization using Taguchi's Technique

For 3 factors at 3 levels Taguchi's L9 Orthogonal array was used for experimentation. The microhardness values and S/N ratio values after carrying out the experiment as per L9 Orthogonal array plan are tabulated in Table 3.

Table 3: Taguchi's L9 Experimentation Plan with Factors and Levels with Microhardness and S/N Ratio Values

wt. %	Sonication Time (minutes)	Curing Time (days)	Microhardness (HV)	SNRA1
1	5	3	8.76	18.85
3	15	3	13.28	22.46
5	10	3	14	22.92
1	10	5	11.11	20.91
3	5	5	11.16	20.95
5	15	5	11.30	21.06
1	15	7	8.8	18.89
3	10	7	12.426	21.89
5	5	7	12.64	22.03

The main effects plot in Figure 6 shows the effect of different factors on the S/N ratio, which is identical with the main effects plot of mean of microhardness shown in Figure 7. From Figure 7, it can be seen that, microhardness increases with an increase in nanoclay concentration. As nanoclay concentration increases from 1 to 3 wt.%, microhardness enhances by 28.6%, which can be calculated from Table 4. As nanoclay concentration increases from 3 to 5 wt.%, microhardness enhances only by 2.9%, which may be due to the initiation of poor dispersion and agglomeration of nanoclay [12]. Overall, as nanoclay concentration increases from 1 to 5 wt.%, there is improvement of 74.2% in microhardness. As sonication time increases from 1 to 3 wt.%, microhardness increases by 15.3%. However, when increasing sonication time beyond 10 minutes, it has a negative influence on microhardness. This may be due to agglomeration of nanoparticles due to too much collision between the nanolayers as more energy is supplied in the form of higher sonication time. As far as curing time is considered, maximum microhardness is observed at first level itself, i. e., 3 days. From Table 4, it can be observed that the difference in microhardness between first and third level is maximum for nanoclay concentration followed by sonication time and curing time. Therefore, nanoclay concentration is the most influencing factor followed by sonication time and curing time.

Table 4: Response Table for Means of Microhardness at Three Levels

Level	Nanoclay Concentration (wt.%)	Sonication Time (minutes)	Curing Time (days)
1	9.557	10.853	12.013
2	12.290	12.513	11.190
3	12.647	11.127	11.290
Delta	3.090	1.660	0.823
Rank	1	2	3

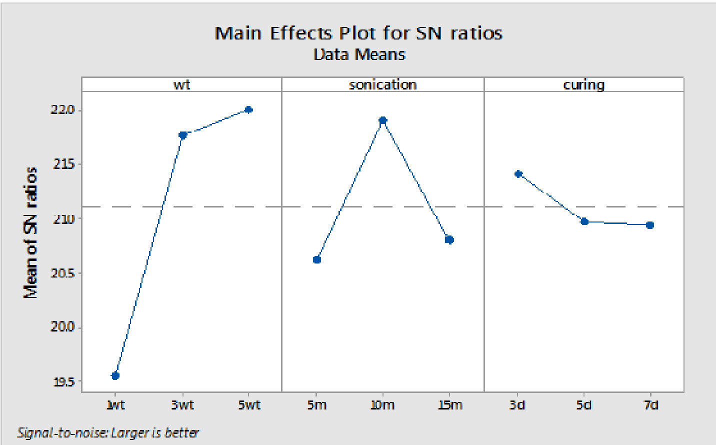

Figure 6: Main Effects Plot of Mean of S/N Ratio (Larger is Better).

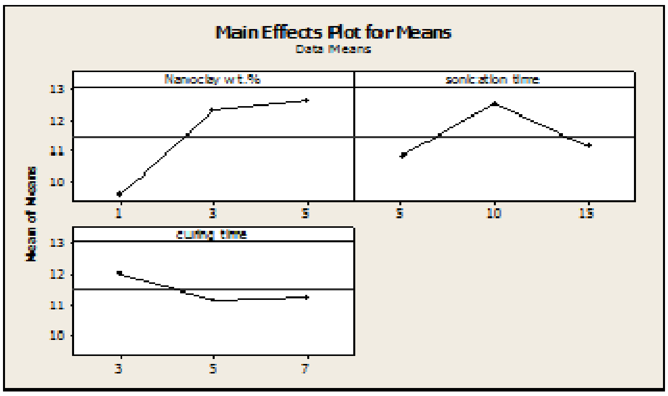

Figure 7: Main Effects Plot of Mean of Microhardness.

From the Figures 6 and 7 it can be concluded that the optimum values of the input factors are 5 wt.% of nanoclay concentration, 10 minutes of sonication time and 3 days of curing time. These values of input factors were one among the 9 experiments in the L9 orthogonal array. Therefore confirmation experiment was not needed.

Contour Plots

Figures 8–10 show the contour plots of two factors at a time vs. microhardness.

From the Figure 8, it can be observed that microhardness in the range of 9–11 is obtained when nanoclay concentration is between 1 and 3 wt.% and sonication time is between 5 and 15 minutes. Microhardness is at a higher range i. e. above 13 when nanoclay concentration is between 3 and 5 wt.% and sonication time is between 5 and 15 minutes. However, maximum microhardness is obtained when nanoclay concentration is 5 wt.% or slightly less than that and for sonication time in and around 10 minutes.

From figure 9, it can be observed that the microhardness in the range of 9–11 is obtained when nanoclay concentration is between 1 and 2 wt.% and curing time is between 3 and 7 days. Microhardness is at a higher range i. e. above 13 when nanoclay concentration is between 3 and 5 wt.% and curing time is slightly on and above 3 days. However, maximum microhardness is obtained when nanoclay concentration is greater than 4 wt.% and for curing time of 3 days.

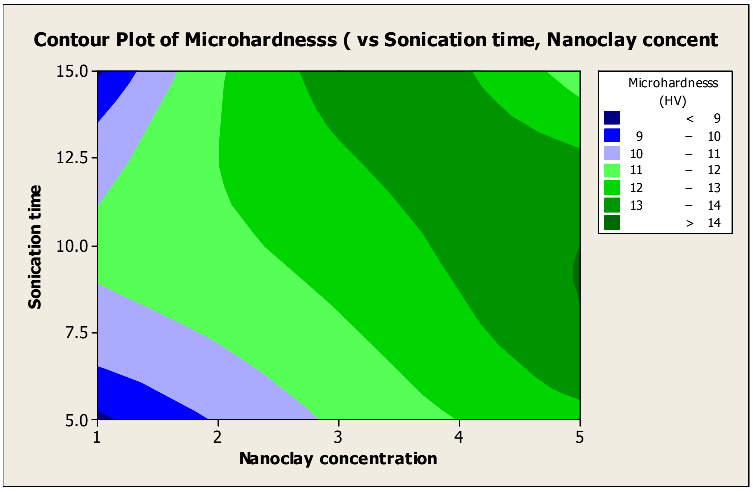

Figure 8: Contour Plot of Nanoclay Concentration vs. Sonication Time.

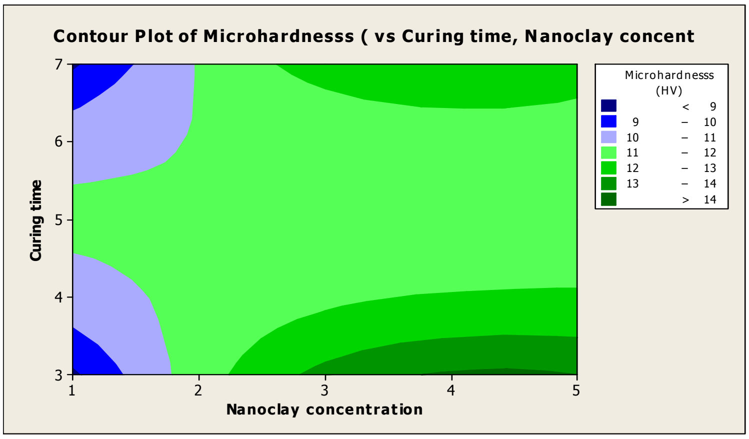

Figure 9: Contour Plot of Nanoclay Concentration vs. Curing Time.

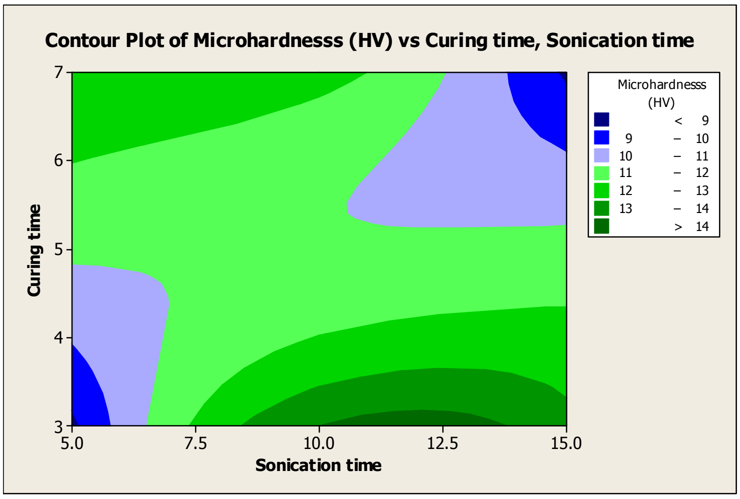

Figure 10: Contour Plot of Nanoclay Concentration vs. Curing Time.

From the figure 7, it can be observed that microhardness is maximum or at higher range when sonication time is atleast 10 minutes and curing time is atleast 3 days.

Regression Analysis

Regression analysis was carried out for the obtained output data and the regression equation is given in equation 2.

$$\text{Microhardness (HV)} = 9.81 + 0.772 \text{ Nanoclay wt.\%} + 0.027 \text{ sonication time} - 0.181 \text{ curing time} \quad (7)$$

It can be clearly observed that, the major influencing input factor is nanoclay concentration (wt.%). Also, it can be observed that the microhardness value is always above (9.81 – 0.181 × curing time), which is for a neat coating. As nanoclay concentration and sonication time increases, the value of microhardness automatically increases.

Study on Sliding Wear Resistance

Wear tests were performed on a clear coating and epoxy with nanoclay concentrations of 1 wt.%, 2 wt.%, 3 wt.%, 4 wt.% and 5 wt.% and their readings are shown from Tables 5 to 10.

Table 5: Pin on Disc Wear Test Readings on Clear Coating

Trial. No	Load (N)	Speed (RPM)	Time (min)	Track diameter (mm)	Initial weight (gm)	Final weight (gm)	ΔW (gm)	Specific Wear Rate W in mm^3/N-m
1	5	100	4	60	11.734	11.730	0.004	10.608×10^{-3}
2	5	100	4	60	11.735	11.731	0.004	
3	5	100	4	60	11.736	11.732	0.004	
4	5	100	4	60	11.734	11.730	0.004	

Using equation (4) and (5) it can be determined that,

Wear rate = 53.4×10^{-3} mm^3/m and wear resistance = 18.72 m/mm^3

Table 6: Pin on Disc Wear Test Readings on 1 wt.% Clay Epoxy Nanocomposite Coating

Trial. No	Load (N)	Speed (RPM)	Time (min)	Track diameter (mm)	Initial weight (gm)	Final weight (gm)	ΔW (gm)	Specific Wear Rate W in mm^3/N-m
1.	5	100	4	60	11.794	11.790	0.004	9.28×10^{-3}
2.	5	100	4	60	11.753	11.750	0.003	

3.	5	100	4	60	11.782	11.779	0.003	
4.	5	100	4	60	11.764	11.760	0.004	
							Avg.= 0.0035	

Wear resistance = 21.55 m//mm3

Table 7: Pin on Disc Wear Test Readings on 2 wt.% Clay Epoxy Nanocomposite Coating

Trial. No	Load (N)	Speed (RPM)	Time (min)	Track diameter (mm)	Initial weight (gm)	Final weight (gm)	ΔW (gm)	Specific Wear Rate W in mm^3/N-m
1.	5	100	4	60	11.766	11.764	0.002	5.968×10^{-3}
2.	5	100	4	60	11.753	11.751	0.002	
3.	5	100	4	60	11.774	11.771	0.003	
4.	5	100	4	60	11.750	11.748	0.002	
							Avg.=0.0025	

Wear resistance = 33.51 m/mm3

Table 8: Pin on Disc Wear Test Readings on 3 wt.% Clay Epoxy Nanocomposite Coating

Trial. No	Load (N)	Speed (RPM)	Time (min)	Track diameter (mm)	Initial weight (gm)	Final weight (gm)	ΔW (gm)	Specific Wear Rate, W in mm^3/N-m
1.	5	100	4	60	11.745	11.743	0.002	4.641×10^{-3}
2.	5	100	4	60	11.806	11.805	0.001	
3.	5	100	4	60	11.744	11.742	0.002	
4.	5	100	4	60	11.752	11.750	0.002	
							Avg.=0.00175	

Wear resistance = 43.09 m/mm3

Table 9: Pin on Disc Wear Test Readings on 4 wt.% Clay Epoxy Nanocomposite Coating

Trial. No	Load (N)	Speed (RPM)	Time (min)	Track diameter (mm)	Initial weight (gm)	Final weight (gm)	ΔW (gm)	Specific Wear Rate, W in mm^3/N-m
1.	5	100	4	60	11.751	11.749	0.002	3.97×10^{-3}
2.	5	100	4	60	11.774	11.772	0.002	
3.	5	100	4	60	11.764	11.763	0.001	
4.	5	100	4	60	11.758	11.757	0.001	
							Avg.=0.0015	

Wear resistance = 50.37 m//mm3

The wear resistance remained same even for 5 wt.% clay epoxy nanocomposite coating. Figure 8 shows the graph showing the variation of wear resistance as a function of nanoclay concentration. It can be observed that as nanoclay concentration increases, wear resistance increases and this happens till 4 wt.%. After that due to clay agglomeration the wear resistance remains constant. The improvement in wear resistance when compared with that of neat coating is 169%.

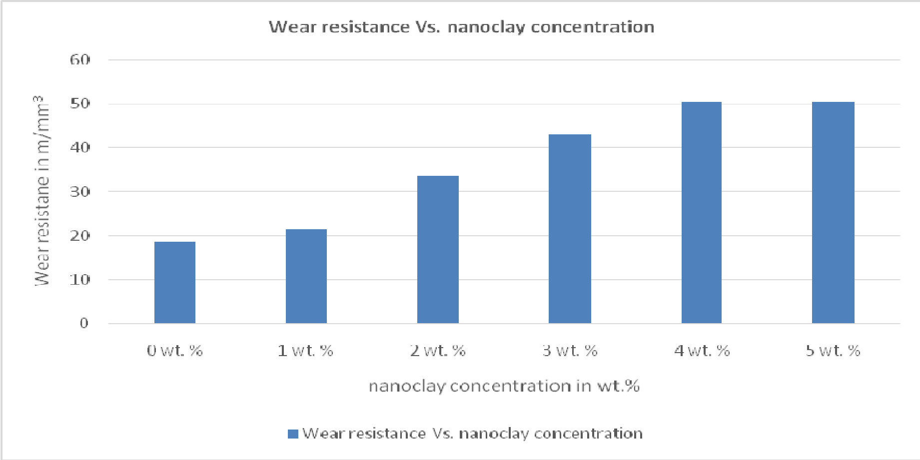

Figure 8: Variation of Wear Resistance as a Function of Nanoclay Concentration.

CONCLUSIONS

It was proven from two sets of experiments that the substrate effect is nil for epoxy clay nanocomposite coating of thickness 200 microns and higher. Using Taguchi's L9 orthogonal array it was found out that, nanoclay concentration was the most significant factor followed by sonication time and curing time. The optimum values of control factors were 5 wt. % of nanoclay, 10 minutes of sonication time and 3 days of curing. The regression analysis led to the development of linear equation containing constant and all the three factors with its coefficients. The wear resistance increases with increase in nanoclay concentration till 4 wt.%, beyond which it saturates due to clay agglomeration. The maximum improvement in wear resistance is 169%.

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